Propane Oxidation at High Pressure and Intermediate Temperatures

Hashemi, Hamid; Christensen, Jakob Munkholt; Glarborg, Peter

Publication date:
2017

Document Version
Peer reviewed version

8TH EUROPEAN COMBUSTION MEETING 2017
APRIL 18 - 21, 2017
DUBROVNIK, CROATIA

Technical University of Denmark DTU

Propane Oxidation at High Pressure and Intermediate Temperatures

Hamid Hashemi, Jakob M. Christensen, Peter Glarborg

Department of Chemical Engineering, Technical University of Denmark (DTU), DK-2800 Kgs. Lyngby, Denmark
Email: pgl@kt.dtu.dk (P. Glarborg), hah@kt.dtu.dk (H. Hashemi)

Motivations

- Propane: a major component in LPG
- Propane: a minor but sensitive component of natural gas
- Engines and gas turbines: need experimental data at high pressures and intermediate temperatures

Experimental: laminar flow reactor

- Quartz reactor to minimize surface reactions
- Steel pressure shell to achieve high pressures
- Temperature: 500—900 K
- Pressure: 100 bar
- Isothermal Zone Length: 42—44 cm
- Residence time: 8—11 s
- Measurement via GC

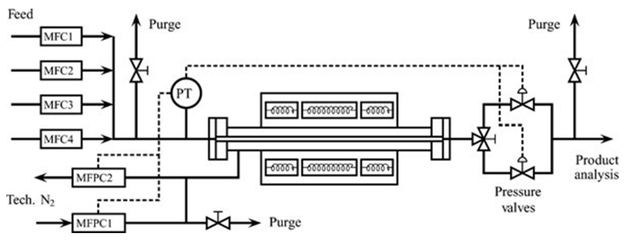

Fig 2. Schematic diagram of the high pressure laminar flow reactor

Chemical kinetics model

- H_2/CO/HC's subsets from recent work by Glarborg et al. [1—4].
- C_3 subset is reviewed and introduced in the present work.
- Low temperature sequences for propane oxidation is adopted from Goldsmith et al. [5].

Results: fuel-rich mixture

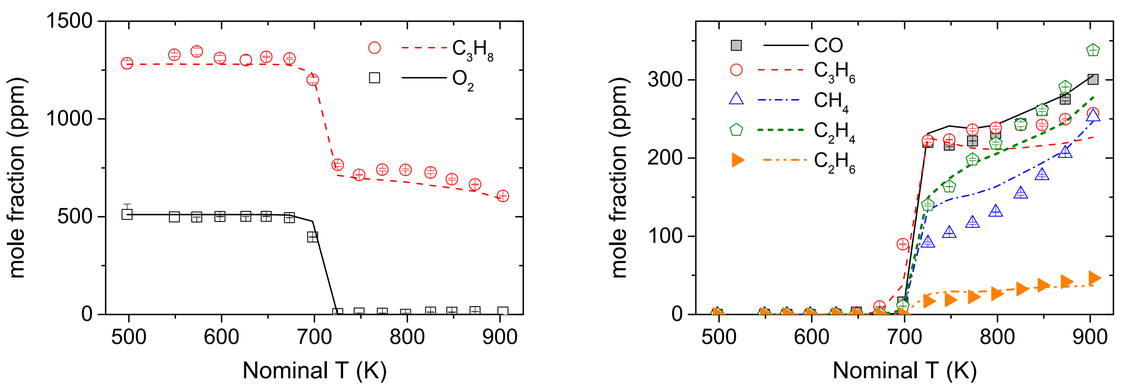

Fig 3. Results of experiments under reducing conditions (1285 ppm C_3H_8 and 511 ppm O_2 in N_2, Φ=12.5) at 100 bar pressure.

The fuel oxidation started at 700–725 K for a fuel-rich mixture (reducing conditions), and the major detected products have been CO, C_3H_6, CH_4, and C_2H_4. The model was able to reproduce the onset of oxidation as well as the concentrations of intermediate components precisely.

Results: stoichiometric mixture

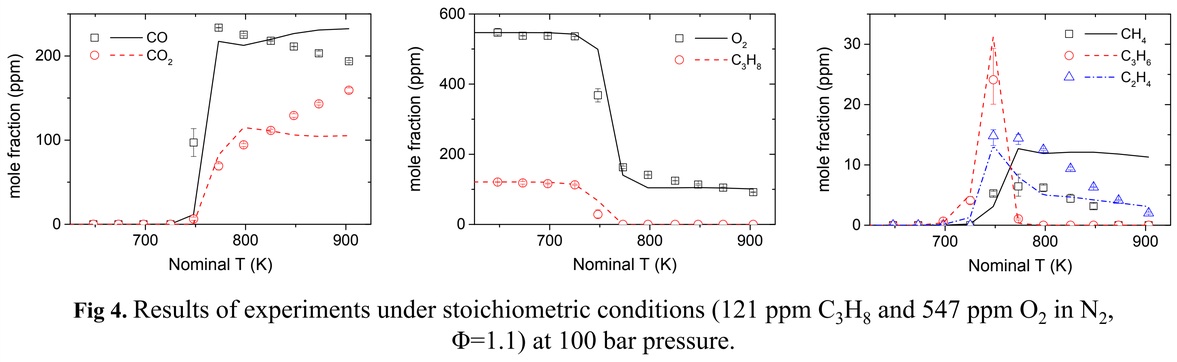

Fig 4. Results of experiments under stoichiometric conditions (121 ppm C_3H_8 and 547 ppm O_2 in N_2, Φ=1.1) at 100 bar pressure.

For a stoichiometric mixture, the fuel conversion started around 725 K. At T>750 K, propane was oxidized almost completely. The major products of the oxidation were CO and CO_2 and the concentration of propene and ethene decreased sharply at T>775 K. The model captured the onset temperature of ignition accurately but it seems that CO oxidation to CO_2 at high temperatures was not precisely captured by the model.

Results: fuel-lean mixture

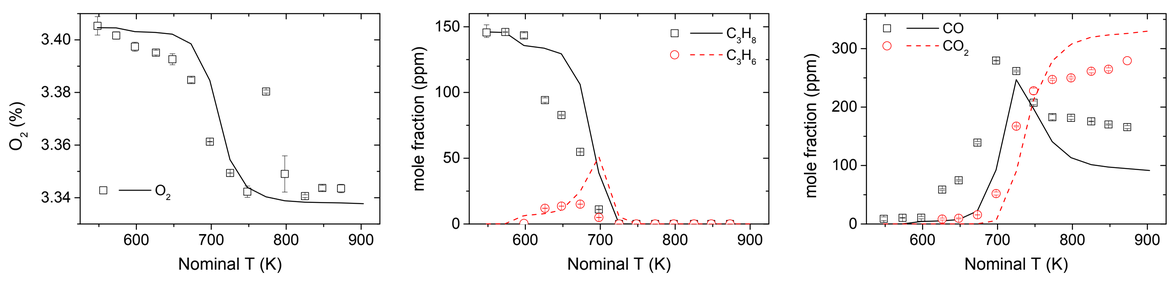

Fig 5. Results of experiments under oxidizing conditions (146 ppm C_3H_8 and 3.405% O_2 in N_2, Φ=0.02) at 100 bar pressure.

Propane concentration dropped sharply at T>600 K for a fuel-lean mixture (oxidizing conditions), and propane vanished from the exhaust at T>725 K. The model predicted slower reactivity compared to the experiments, so the fuel conversion was slightly underpredicted by the model.

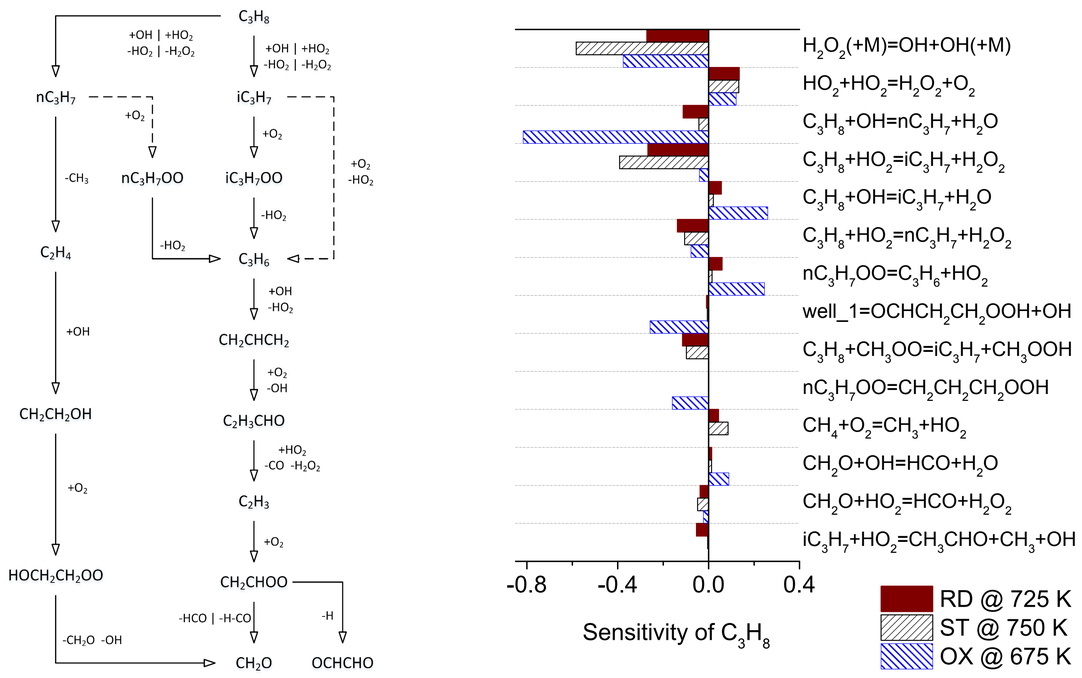

Fig 6. ***Left:*** Reaction pathways for propane oxidation under stoichiometric conditions (750 K, 100 bar). ***Right:*** Sensitivity of C_3H_8 prediction under flow-reactor conditions (RD: reducing, ST: stoichiometric, OX: oxidizing conditions) at 100 bar. The component $HOOCH_2CH_2CH_2OO$ is named "well_1" in above.

According to the results of sensitivity analyses, propane oxidation is largely controlled by H-abstraction by HO_2 from propane (R1). The branch leading to iC_3H_7 shows a larger sensitivity compared to the other one (except for oxidizing conditions). The reaction between C_3H_8 and OH (R2) is also sensitive. While the branch to nC_3H_7 promotes the oxidation, the other branch to iC_3H_7 inhibits the fuel conversion. The H-abstraction by CH_3OO from propane (R3) is also sensitive for reducing and stoichiometric conditions.

$C_3H_8 + HO_2 = nC_3H_7 + H_2O_2$ (R1a)
$C_3H_8 + HO_2 = iC_3H_7 + H_2O_2$ (R1b)
$C_3H_8 + OH = nC_3H_7 + H_2O$ (R2a)
$C_3H_8 + OH = iC_3H_7 + H_2O$ (R2b)
$C_3H_8 + CH_3OO = iC_3H_7 + CH_3OOH$ (R3)

Analysing the reaction pathway of propane oxidation revealed that for stoichiometric conditions and at 750 K, the major path for propane oxidation begins with H-abstraction by OH and HO_2 (R1 & R2). If the H-abstraction results in an iC_3H_7 radical, it will add to molecular oxygen to give iC_3H_7OO, which later decomposes to propene. If R1 and R2 yield nC_3H_7, then decomposition to ethene is favoured compared to addition of nC_3H_7 to molecular oxygen.

Summary

Propane oxidation at intermediate temperatures (500—900 K) and high pressure (100 bar) has been characterized by conducting experiments in a laminar flow reactor over a wide range of stoichiometries. The onset of fuel oxidation was found to be 600—725 K, depending on mixture stoichiometry. The model agreed well with the measurements of fuel-rich and stoichiometric mixtures while the model underpredicted the fuel conversion for fuel-lean conditions. Sensitivity analyses revealed the importance of H-abstraction reactions by HO_2, OH, and CH_3OO in controlling propane oxidation at 750 K.

References

[1] H. Hashemi, J. M. Christensen, S. Gersen, P. Glarborg, *"Hydrogen oxidation at high pressure and intermediate temperatures: Experiments and kinetic modeling"*, Proc. Combust. Inst. 35 (2015) 553—560.

[2] H. Hashemi, J. M. Christensen, S. Gersen, H.B. Levinsky, S.J. Klippenstein, P. Glarborg, *"High-pressure oxidation of methane"*, Combust. Flame 172 (2016) 349—364.

[3] J. Lopez, C. Rasmussen, H. Hashemi, M. Alzueta, Y. Gao, P. Marshall, C. Goldsmith, P. Glarborg, *"Experimental and kinetic modeling study of C_2H_2 oxidation at high pressure"*, Int. J. Chem. Kinet. 48 (2016) 724—738.

[4] H. Hashemi, J.G. Jacobsen, C.T. Rasmussen, J.M. Christensen, P. Glarborg, S. Gersen, M. Essen, H.B. Levinsky, S.J. Klippenstein, *"High-pressure oxidation of ethane"*, Combust. Flame (2017), accepted.

[5] C. F. Goldsmith, W. H. Green, S. J. Klippenstein, *"Role of O_2 + QOOH in low-temperature ignition of propane. 1. Temperature and pressure dependent rate coefficients"*, J. Phys. Chem. A 116 (2012) 3325—3346.